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Review

Production, separation and applications of phenolic-rich bio-oil – A review

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HIGHLIGHTS

- This paper provides an overview of current research trend of phenolic-rich bio-oil.
- Various production methods for phenolic-rich bio-oil by pyrolysis are provided.
- Recent approaches for the separation of bio-oil are presented.
- Application of phenolic compounds in the synthesis of phenol resins is discussed.

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ABSTRACT

This paper provides an overview of current research trends in the production and separation of phenolic-rich bio-oils, as well as their applications. The first part of this paper highlights the strong dependency of the phenolic content of bio-oil on the kinds of biomass feedstock, reaction system, reaction conditions, and the type of catalysts used in their production. More recent separation technologies are also discussed in the second part of the paper. The final part of the paper deals with recent experimental results from applications of phenolic-rich bio-oils in the synthesis of phenolic resins. The paper suggests that the microwave-assisted pyrolysis of palm residues is a promising route for phenolic-rich bio-oil production, and that the use of supercritical CO_2 and switchable hydrophilicity solvents during extraction, as well as molecular distillation techniques, can be applied to increase the recovery of phenolic compounds from bio-oils.

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1. Introduction

Pyrolysis is one of the principal conversion technologies which are used to extract bioenergy from biomass in an eco-friendly and cost-effective manner. Bio-oils derived from biomass pyrolysis can be used directly as fuel oils in boilers and furnaces without any upgrading. However, bio-oils contain a relatively high amount of oxygenates, which results in undesirable fuel properties, such as high viscosity and corrosiveness, low heating value, and instability. Due to the relatively low fuel values of bio-oils, they cannot directly replace high-grade fuels such as gasoline or diesel, and hence, cannot fuel transportation. In order to explore the feasibility of bio-oil as a high-grade fuel, there has been intensive research on the upgrading of bio-oils to higher fuel value hydrocarbons, mainly through the use of hydrodeoxygenation (HDO) and catalytic fast pyrolysis, which have been applied mainly since the mid-2000s. The current status of research on HDO and catalytic fast pyrolysis is well represented by a small number of papers (Choudhary and Phillips, 2011; Liu et al., 2014; Ruddy et al., 2014). Although these intensive efforts to upgrade bio-oils have resulted in considerable progress, there are still a number of technical barriers to overcome, such as catalyst deactivation and increasing the yield of hydrocarbons for zeolites, short catalyst lifetime and the additional supply of hydrogen which is required for HDO (Mortensen et al., 2011). Meanwhile, it is not necessarily optimal to simply convert bio-oils to fuels, as bio-oils contain commodity and specialty chemicals. Hence, the isolation of these chemicals is an additional consideration of biomass pyrolysis. Accordingly, a number of studies have been performed either to investigate mechanism and kinetics for the formation of such chemicals, to optimize reaction conditions for chemical production, or to separate a specific chemical from bio-oils. (Ranzi et al., 2008; Teella et al., 2011; Oh et al., 2013). These studies have repeatedly shown that the recovery of chemicals by pyrolysis has a number of drawbacks, including low contents of such chemicals in bio-oil, and high costs of bio-oil separation, etc. Nevertheless, the application of various catalysts and the continuous development of separation technologies are

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stimulating the research area of the chemical recovery from the biomass pyrolysis. In particular, phenolic compounds of bio-oil have a wide range of use within industry, and can often be directly applied without any intensive separation procedures. A few previous studies have provided a good overview of the phenolic compounds arising from biomass pyrolysis (Amen-Chen et al., 2001; Effendi et al., 2008).

This review focuses on the more recent studies of phenolic compounds arising from biomass pyrolysis. In particular, this study provides an overview of the production, separation and application of phenolic compounds.

2. Bio-oil, chemicals, phenolic compounds and separation technologies

2.1. Chemicals in bio-oil and their quantification

2.1.1. Chemicals in bio-oil

Bio-oil is a complex mixture of water (15–30 wt%), and organic compounds. The addition of water to bio-oil gives rise to an aqueous-organic phase separation. If a phase separation procedure involves the addition of drops of bio-oil to a large amount of water, followed by filtration and drying of the filtrate, and the resulting powder is commonly referred to as a pyrolytic lignin, containing lignin-derivative oligomers (Czernik and Bridgewater, 2004). Bio-oils contain a broad range of organic chemicals, including a range of high-value bio-chemicals, such as levoglucosan. Hence, there is potential for the extraction and use of a range of chemicals from bio-oils as renewable feedstocks for a broad range of chemical industries. The quantities of the various bio-oil components are strongly dependent on the feedstock composition, production method, and reaction conditions. Table 1 shows typical components of bio-oils produced from different biomass feedstocks.

2.1.2. Quantification of bio-oil components

Bio-oils produced by the pyrolysis of lignocellulosic biomass contain over 400 different chemical compounds. These compounds can be classified into the primary categories of organic acids, aldehydes, ketones, furans, sugar based components, and phenolic compounds. The diversity and complexity of bio-oils make the accurate analysis of their specific chemical composition a very complicated task. Such analysis of bio-oil typically utilizes gas chromatography–mass spectroscopy (GC–MS), chromatography-flame ionization detector (GC-FID), high-performance liquid chromatography, ion-exchange chromatography, and/or nuclear magnetic resonance (NMR) spectroscopy. In particular, hyphenated techniques, such as GC–MS are considered to be the more appropriate methods for the analysis of more complex mixtures. However, limited chemical information can be obtained from conventional GC–MS analysis of bio-oils due to the large number of compounds and co-elutions contained therein (Tessarolo et al., 2013). Recent advances in the analysis of bio-oils, such as comprehensive two-dimensional gas chromatography, have led to the enhancement of their qualitative analysis. In particular, the use of a time-of-flight mass spectrometer has led to a dramatic improvement in the separation and identification of complex mixtures. However, the quantitative determination of bio-oil components remains a tedious and expensive analytical procedure, largely due to the requirement for multiple-calibrations of a plethora of chemicals, and the individual expenses associated with their supply, management and maintenance. Therefore, the absence of an all-encompassing quantitative method for the chemical analysis of bio-oils remains. As with most other complex materials, the vast majority of papers focus on semi-quantitative analysis of bio-oil, or on the more detailed analysis of a single component/group of components.

Table 1
Typical bio-oil components derived from different biomass at different reaction conditions.

Components	Poplar wood (500 °C), wt% mf feed (Scott et al., 2000)	Hardwood chip (550 °C), area% (Dobele et al., 2007)	Maize stalk (445 °C), wt% (Zheng, 2008)
Sugars			
Levoglucosan	3.0	1.6	
Other sugars	5.7		
Alcohols, aldehydes		9.3	
Hydroxyacetaldehyde	10.0		
Glyoxal	2.2		
Acids, ester		20.2	
Acetic acid	5.4		2.7
Butyric acid			1.5
Ketones			
Dihydroxyacetone			3.9
Ethers			
Pyrans		1.5	
Furans		6.6	2.4 (acetyl furan)
Phenolic compounds			
Phenol			1.4
Guaiacol			2.5
Pyrolytic lignin	16.2		

mf: moisture free.

2.2. Phenolic compounds

Phenolic compounds found in bio-oils are composed of both simple phenols consisting chiefly of a singly substituted phenolic ring with alcohol, aldehyde or carboxylic acid groups and oligomeric polyphenols having multiples of phenol structural units, each of which being products of lignin decomposition. Lignin is one of the primary components of dry wood, accounting for 18–40 wt% of the total mass, depending on the species of wood (Amen-Chen et al., 2001). Lignin is a very complex macromolecular compound, and is composed of monomeric phenylpropanoid units known as syringyl-, guaiacyl-, and p-hydroxyphenyl, originating from three monolignol monomers which differ in their degree of methoxylation; p-coumaryl, coniferyl, and sinapyl alcohols. In softwood lignin, coniferyl alcohol is the predominant building unit, while in hardwoods the ratio of coniferyl/synapyl shows considerable variation. Therefore, the pyrolysis of softwood lignins yields mainly guaiacols, whereas hardwood lignins give both guaiacols and syringols (Brebu and Vasile, 2010). Lignin thermally decomposes over a broad temperature range, covering the 160–900 °C region (Yang et al., 2007). Evans et al. proposed a possible free radical mechanism for the pyrolysis of lignin. According to this mechanism, alkyl hydroxyl groups in the α-position are first eliminated from the propane side chain, followed by a β-ether cleavage (Evans et al., 1986). Liu et al. confirmed the readiness of β-ether cleavage by a quantum chemistry calculation in their study on the guaiacyl type lignin model compound, drawing a comparison with the $C_\alpha - C_\beta$ cleavage of the propane side chain (Liu et al., 2011). After β-ether cleavage, monolignol monomers are produced, which may be further degraded at different positions of the propane side chain, yielding a variety of simple phenols. Hydrogen transfer at the γ-position to free radical species can produce formaldehyde, dimers and methoxyphenols. Recently, Shen et al. investigated the formation of a number of common products from the pyrolysis of kraft lignin. They found that guaiacols and syringols were mostly produced by the cracking of the side-chain of the lignin monomeric units in parallel to the cleavage of the α- or β-4-aryl ether linkage. They also acted as precursors for the formation of phenol-, cresol- and catechol-types through the corresponding cracking mode of the methoxy group on the aromatic rings (Shen et al., 2010).

2.3. Separation technologies for bio-oil components

The recovery of chemicals from bio-oil has typically been carried out using conventional separation technologies, such as solvent extraction, column chromatography, and distillation. Advancement of the separation of bio-oil components has recently been made by applying new apparatus and media. This section provides an overview of bio-oil separation technologies. Details of recent developments on the separation of phenolic compounds from bio-oil will be provided in the next section.

2.3.1. Solvent – and supercritical fluid extraction

Solvent extraction is a process which selectively dissolves target components of a mixture of components into a solvent for which those components have a greater affinity. Commonly used solvents for the extraction of specific compounds from bio-oil include water, alcohols, ethyl acetate, hydrocarbons such as toluene and n-hexane, ethers, ketones, dichloromethane, and alkaline solutions. In solvent extraction procedures, large volumes of solvents are required, making the industrialization of some extractions unfeasible. In recent years, supercritical fluid extraction (SFE) has been applied for the separation of bio-oil components, and this process is generally carried out at low temperatures, preventing undesirable reactions of bio-oil components. The technology has several advantages over other conventional extraction methods: (1) it is flexible due to the possibility of continuous modulation of the solvent power/selectivity of the supercritical fluid, (2) it allows for the elimination of polluting organic solvents and removes the requirement for expensive solvent removal from the extracts (Reverchon and De Marco, 2006). Several solvents have been studied for their potential use as SFE solvents. However, CO_2 is the most popular SFE solvent, due to its non-toxic and non-flammable characteristics, as well as its low cost in a high purity form. In a study of the supercritical CO_2 extraction of bio-oil, valuable compounds, such as furanoids, pyranoids and benzenoids could be enriched into the extracted fraction, while water could be efficiently removed after extraction (Naik et al., 2010).

2.3.2. Column chromatography

The separation of bio-oil components through column chromatography commonly utilizes silica gel and aluminum oxide as the stationary phase, where the mobile phase is selected according to the polarity of bio-oil components which are to be extracted. The separation is based on the different adsorption capabilities of bio-oil components onto the stationary phase. Column chromatography can economically separate bio-oil, but its low throughput makes it only suitable for high value-added compounds. In one study, it was found that hazardous phthalate esters could be separated from bio-oil using column chromatography (Zeng et al., 2011).

2.3.3. Distillation

Distillation separates bio-oil components according to their different volatilities. Atmospheric pressure-, vacuum-, steam-, and molecular distillation can be applied to bio-oil separation. Czernik and Bridgwater reported that the boiling of bio-oil started below 100 °C under atmospheric pressure, and that distillation was stopped at 280 °C, leaving 35–50 wt% of the starting material as a residue (Czernik and Bridgewater, 2004). In contrast to atmospheric pressure distillation, vacuum distillation has a strong advantage, in that it operates at much lower temperatures. The distilled organic fraction from vacuum distillation contained almost no water and fewer oxygenated compounds, although the method uses large amounts of energy. Steam distillation, which requires a relatively large initial capital investment, can be applied for the separation of bio-oil components, introducing steam into the distilling column to heat bio-oil and decrease its viscosity. With the addition of steam, the organic-water mixture (bio-oil) boils at a lower temperature (below 100 °C), allowing thermally sensitive compounds to be separated with reduced decomposition. Molecular distillation, which is widely applied in petrochemical, fine chemical, medicine, pharmaceutical, and food-processing industries, is also considered to be an appropriate process for the separation of thermally unstable bio-oils. Conventional distillation technologies separate components based on the differences in their boiling points. However, the principle of molecular distillation (or short-path distillation) is based on the various mean free paths of different molecules. Compared to other forms of distillation, molecular distillation has the advantages of lower operating temperatures, shorter heating time, higher separation efficiencies and minimal losses by thermal decomposition. In a study of the separation of bio-oil using molecular distillation, a maximum distillate yield of 85% was obtained without coking or polymerization (Wang et al., 2009). The main disadvantage of molecular distillation lies in the high costs of equipment.

3. Recent developments in the production, separation, and application of phenolic-rich bio-oil

3.1. Production of phenolic-rich bio-oil by pyrolysis

This section covers the production of phenolic compounds by catalytic and non-catalytic pyrolysis of biomass. The contents of phenol and phenolic compounds in bio-oil are separately considered here.

3.1.1. Non-catalytic pyrolysis

The base of all phenolic compounds is phenol, which is highly reactive in the synthesis of phenolic resins. Other monomeric phenolic compounds (or simple phenols) in bio-oil, such as cresol and vanillin, are also very valuable chemicals. Oligomeric polyphenols contain varying numbers of functional groups, and constitute the majority of phenolic compounds contained within typical bio-oils. The molecular weight of the oligomers generally ranges from several hundred to 5000 g/mol, and they can form a network due to intermolecular interactions (Effendi et al., 2008). Oligomeric polyphenols (or pyrolytic lignin) can be used, for instance, in the synthesis of phenol resin. The concentrations of phenolic compounds in bio-oil derived from non-catalytic biomass pyrolysis are strongly dependent on the kinds of biomass feedstock, pyrolysis operation conditions, and pyrolysis reaction systems.

3.1.1.1. Types of biomass feedstock. Different types of biomass contain different amounts and types of ingredients. The content and chemical structure of lignin in biomass appears to be the main factor influencing the composition of phenolic compounds. Typical biomass feedstocks used for the production of phenolic-rich bio-oil have been wood and lignin-based biomass waste. The non-catalytic pyrolysis of wood feedstocks typically yields a low content of phenol. Diebolt reported phenol contents of 0.1–3.8 wt% in bio-oils (Diebold, 2003). Luo et al. performed GC–MS analysis of bio-oil derived from the pyrolysis of wood and rice straw in a fluidized bed reactor, and identified phenolic compounds up to 20 area% of the bio-oil (Luo et al., 2004). Lignin-based biomass waste has been a very attractive feedstock for phenolic-rich bio-oils, largely due to the fact that it can be obtained at a negligible cost from the residues of pulp from the paper industry, or from residues obtained from biofuel production using lignocellulosic biomass feedstocks. In spite of the reduced costs and environmental impacts associating with this material, the heterogeneity of the material as well as the inherent recalcitrance of lignin still discourage its application for the commercial production of valuable secondary compounds. Due to its thermal recalcitrance, the pyrolysis of lignins (kraft lignin, klason lignin, and ethanol organosolv lignin) generally gives rise to bio-oil yields of just 20–40 wt% (Mu et al., 2013). Recently, Jiang et al. studied the effect of temperature on the composition of bio-oil in the pyrolysis of Alcell lignin and Asian lignin using pyrolysis-gas chromatography–mass spectrometry. In their work, the maximum yield (17.2 wt% for Alcell lignin and 15.5 wt% for Asian lignin) of phenolic compounds was obtained at 600 °C for both lignins (Jiang et al., 2010). They concluded that reactions, such as demethylation, demethoxylation, decarboxylation, and alkylation, occurred at higher temperatures, producing alkylphenols and polyhydroxybenzene. De Wild *et* al. conducted the fast pyrolysis of Alcell lignin and Asian lignin at 400 °C using a fluidized bed reactor, and yielding up to 21 wt% (on a dry basis) of a condensable fraction containing 10 wt% (on a dry basis) of phenols (De Wild et al., 2009). In another study of De Wild et al. conducted also using a fluidized bed reactor, bio-oils obtained from the pyrolysis of organosolv lignins were found to contain approximately 45 wt% oligomeric phenolic substances, 23 wt% monomeric phenols, and 33 wt% water (De Wild et al., 2014). Agricultural residues were one of the biomass feedstocks used for the production of second generation biofuels or biochemical by pyrolysis. Yanik et al. carried out the fast pyrolysis of three agricultural wastes (corncob, straw and oreganum stalks) at 500 °C in a fluidized bed reactor. They performed GC–MS analysis of the water-soluble fractions (around 52–68 wt% of the bio-oils), and the contents of simple phenols were about 1.0–2.4 wt% (Yanik et al., 2007). Imam and Capareda characterized the bio-oil obtained from the pyrolysis of switchgrass, and reported that mono-, di- and tri-substituted phenolic compounds detected in switchgrass pyrolysis oil amounted to 20.5 area% of the GC chromatogram (Imam and Capareda, 2012). Lately, palm oil residues have gained much attention as a major fuel and chemical source due to the increasing volume of palm oil residue accumulation. Accordingly, a study of the fast pyrolysis of palm oil residues aimed to investigate the potential fuel and chemical production. Kim et al. conducted the pyrolysis of palm kernel shells (PKS), which contained a high lignin content of about 46 wt%, in a fluidized-bed reactor, and reported a maximum bio-oil yield of 49 wt% and that the maximum contents of phenolic compounds in the bio-oil obtained at 475 °C amounted to about 70 area% from the GC-FID analysis. Surprisingly, the phenol content in the bio-oil reached up to 22 area% (Kim et al., 2010). A number of other studies on the pyrolysis of palm residues confirmed the high phenol content in bio-oils from PKS. Asadullah et al. carried out the fast pyrolysis of PKS in a fluidized-bed reactor equipped with a top-feeding system. In the experiments, bio-oil yields were varied between 44 and 56 wt%. The phenol content in their bio-oils reached up to about 20 area% (Asadullah et al., 2013). Bertero et al. conducted the pyrolysis of two palm residues at 550 °C in a fixed bed reactor: the pericarp from white palm fruit and the residuals from the extraction of oil from white palm seeds. They reported yields of bio-oil plus tar from 35 to 44 wt% containing 23–35 and 67–77 wt% of phenols, respectively (Bertero et al., 2014). The high amount of phenol, the base of phenols, in the bio-oils of palm oil residues is very interesting because this phenol, if isolated from the bio-oils, may be used to replace the phenol which is currently obtained from petroleum.

3.1.1.2. Pyrolysis conditions. Bio-oil yields, as well as the content of phenolic compounds contained therein, are strongly dependent on pyrolysis operational conditions, such as pyrolysis temperature, vapor residence time and the presence of oxygen. A study of the pyrolysis of mixed wood waste using a fluidized bed reactor showed that the concentration of phenolic compounds in bio-oil increased as the pyrolysis temperature was increased from 400 to 500 °C, and a further increase in the concentration could not be observed at 550 °C (Horne and Williams, 1999). Hoekstra et al. also investigated the influence of pyrolysis temperature and residence time on the yields of important components of bio-oil using a fluidized bed and tubular reactor placed in series. In the work, they conducted the pyrolysis of pine wood with a low-mineral content in a fluidized bed reactor under fixed reaction conditions, and the temperature and vapor residence time of the tubular reactor were varied. Under such reaction conditions, they found that the yield of phenolic compounds increased from 400 to 550 °C, and that a longer vapor residence time, especially at 550 °C, favored the formation of phenolic compounds (Hoekstra et al., 2012). Butt investigated the influence of molecular oxygen on the yield of phenolic compounds, performing the fast pyrolysis of radiata pine in a fluidized bed reactor at low temperatures (290–295 °C). The study found that the yield of phenolic compounds in bio-oil was strongly dependent on the concentration of oxygen in the carrier gas, changing the phenolic yield from 0.02 (when no oxygen) to 0.64% (when the oxygen concentration was 20%), based on oven-dried or oven-dried and ethanol extracted biomass feedstocks. He postulated that molecular oxygen promoted the depolymerization of radiata pine through a free radical mechanism, whereby it facilitated the formation of free radicals and/or itself behaved as a free radical. The actual phenolic yield was relatively low compared to that obtained from higher temperature processes, due to the reduced biomass residence time and lower reaction temperature employed (Butt, 2006).

3.1.1.3. Pyrolysis reaction systems. The specific type of pyrolysis reaction system also influences the yield of phenolic compounds. There have been many pyrolysis systems applied for biomass pyrolysis over the past few decades. In this paper, discussion on well-known conventional pyrolysis systems will not be given. Instead, the characteristics of some new specific pyrolysis systems for the production of phenolic-rich bio-oils, such as microwave-assisted pyrolysis and stepwise pyrolysis system, will be discussed below. In general, conventional pyrolysis heating systems provide heat to biomass externally by conduction, convection and radiation, and hence, they suffer from heat transfer resistance and heat losses to their surroundings (Salema and Ani, 2011). Because of the slow rate of heating of conventional pyrolysis systems, they cannot avoid undesirable secondary reactions which reduce product quality. In contrast, microwave-assisted pyrolysis of biomass has much higher heating rates due to the direct conversion of the electromagnetic energy into heat, which results in a good product quality through enhanced chemical reactivity and the suppression of secondary reactions (Fernandez et al., 2011). In addition, microwave-assisted pyrolysis of biomass has a strong advantage in that there is no necessity for feedstock shredding, and hence, energy consumption is further reduced. Aziz et al. carried out the pyrolysis of PKS, wood chips and sago wastes using a microwave system under various heating times, and at moderate temperatures ranging from 250 to 390 °C. Bio-oil yields between 4 and 17 wt% could be obtained in the study. An experiment conducted at 289 °C with a heating time of 3 min was determined to be optimal, producing a bio-oil with a phenol content of 31 area% from PKS. The pyrolysis of sago wastes also yielded a bio-oil with a high phenol content (19 area%). In the study, they found that an increase in heating time did not lead to an increase in the phenol content (Aziz et al., 2013). Meanwhile, many studies of microwave-assisted pyrolysis have applied activated carbon as a catalyst, and the experimental results of these studies are presented in the next section. Although above experimental results showed potential of microwave-assisted pyrolysis, microwave-assisted pyrolysis systems must overcome a number of drawbacks, such as high electrical power consumption and high operational costs. Furthermore, if these systems are to become economically feasible industries, a uniform heating of the biomass must be achieved, along with a scaling-up of the microwave-assisted pyrolysis system. Stepwise pyrolysis technology can be used to fractionate bio-oil by pyrolysis. It is based on the fact that the main biomass constituents (hemicelluloses, cellulose and lignin) behave differently under different reaction parameters, such as temperature and heating rate etc. Therefore, the product compositions obtained at each step would be varied, and separation of bio-oil components during pyrolysis could be possible in stepwise pyrolysis. Most application of stepwise pyrolysis to bio-oil has used varying temperature within each study to separate the different fractions. A typical stepwise pyrolysis process consists of a torrefaction and subsequent fast pyrolysis, aiming to produce bio-oils with lower contents of water and acids, and higher concentrations of the desired compounds (Zheng et al., 2012). Murwanashyaka et al. investigated the evolution of phenolic compounds in the stepwise pyrolysis of a mixture of birch bark (ca. 46%) and birch sapwood (ca. 54%) using a laboratory scale batch reactor and a temperature range of 25–550 °C under vacuum (0.7 kPa). The reaction temperature range in their study was divided into five stages, namely 25–200, 200–275, 275–350, 350–450, and 450–550 °C. The hold-time of each stage was 1 h. Most of the mono-phenols (methylguaiacol, ethylguaiacol, guaiacol, propenylsyringol, phenol and catechol) were produced in the temperature range between 275 and 350 °C (Murwanashyaka et al., 2001). Westerhof et al. investigated the influence of temperature on the composition of the bio-oil produced in a stepwise pyrolysis of pine wood using a fluidized bed reactor, where the first step temperature was between 260 and 360 °C. The char obtained from this first step was cooled and then pyrolyzed again at 530 °C. In the experiment, they found that GC detectable phenolic compounds were not collected in the first step, whereas the yield of water-insoluble compounds increased when the first step temperature was increased. When the first step temperature was 260 °C, most of phenolic compounds were collected in the second step (Westerhof et al., 2012). Experimental results reported up to now have shown that stepwise pyrolysis has not achieved a clean separation of the targeted compounds, but it appears to be suitable for concentrating the fractions that they are contained in. In the stepwise pyrolysis, moreover, water can be removed from the feedstock in the first step, and most phenolic compounds can be concentrated in further steps. Isolated phenolic compounds are much more valuable than mixed phenols, and so, stepwise pyrolysis, should aim to incorporate multistage reactors in a cost-effective manner, and to develop operationally stable up-scaled stepwise pyrolysis processes.

3.1.2. Catalytic pyrolysis

Recent catalytic pyrolysis of biomass for the production of phenolic compounds has applied various catalysts, including activated carbon, alkaline catalysts, and K_3PO_4. Initially, catalytic microwave-assisted pyrolysis was intensively been performed by several research groups, using activated carbon as a microwave absorber catalyst. Salema and Ani carried out the pyrolysis of PKS in a 300 and 450 W microwave system using an overhead stirrer and activated carbon, and found that the stirrer speed as well as the amount of activated carbon (microwave absorber) had a crucial impact on the product yield and the properties of the products. In the study, bio-oil yields were below 20 wt%. However, a bio-oil with a high phenol content (72 area%) could be obtained using 50 wt% microwave absorber and a stirrer speed of 200 rpm (Salema and Ani, 2012a). In another work conducted by the same group, using a microwave system with a higher power (800 W) for the pyrolysis of oil palm empty fruit bunch (OPEFB), a bio-oil yield of 28 wt% was obtained using 25 wt% microwave absorber (coconut-based activated carbon) and a stirrer speed of 50 rpm. Phenol was the major chemical in the bio-oil, and it was at its highest content (85 area%) where 75 wt% microwave absorber and a stirrer speed of 100 rpm were applied. As some bio-oils consist almost entirely of phenolic compounds, they may be applied directly to a number of phenolic applications, for instance phenolic resin synthesis (Salema and Ani, 2012b).

Bu et al. carried out the microwave pyrolysis of Douglas fir sawdust pellets, investigating the effects of different kinds of activated carbons (lignite coal based and wood based) on the product yield and chemical compositions of product oil at 400 °C, using a fixed ratio of activated carbon to biomass (3:1). In their work, the addition of activated carbon had significant influence on the phenolic compound content of the bio-oil, though the yield of bio-oil decreased from 45 wt% (non-catalytic) to about 26.5–33.2 wt% (catalytic). A high amount of phenolic compounds in the product oils ($\sim$75 area%) was obtained when wood-based and lignite-coal based activated carbons were applied. The amount of phenol in the bio-oil was 30.4 area% from the pyrolysis with lignite coal activated carbon, whereas 42.5 area% with a wood based activated carbon. They also reported that the selected activated carbon could be reused at least 3–4 times without any significant deactivation (Bu et al., 2013). In another work of Bu et al. on the catalytic microwave pyrolysis of lignin by activated carbons, they reported the bio-oil yield reached up to 42 wt%, and that the bio-oils had a high concentration of phenol (up to 45 area% in the bio-oil) (Bu et al., 2014). Bu et al. also studied the role of activated carbon during microwave-assisted pyrolysis. They proposed a mechanism based on the increased production of H_2 gas when activated carbon was used as the catalyst which could be hot spots under microwave heating. They inferred that the gases, including H_2, generated by gasification reactions aided the decomposition of lignin, promoting the deoxygenation of lignin-derived oil. Finally, phenolic compounds could be produced after a series of reactions such as decarboxylation and dehydration (Bu et al., 2012). Table 2 shows a comparison of the phenol content of bio-oils that were obtained by conventional pyrolysis and microwave-assisted pyrolysis of biomass (both catalytic and non-catalytic).

Table 2 shows that PKS is a very interesting biomass source for the production of renewable phenol, and that a microwave-assisted pyrolysis with activated carbon can lead to a remarkable increase in the phenol content of a bio-oil, compared to the more traditional methodologies. A bio-oil containing a high concentration of phenol appears to be very attractive in the synthesis of phenolic resins compared to other bio-oils that contain low concentration of phenol, due to the high reactivity of phenol toward aldehydes.

Alkaline catalysts, various carbonates like Na_2CO_3, K_2CO_3, and hydroxides such as KOH, NaOH or $Ca(OH)_2$, have been known as active catalysts for the decomposition of lignin, and the conversion of biomass, especially lignin, with such alkaline catalysts has mainly been tested thermally in an aqueous medium (Zhou et al., 2011). Recently, several studies have been performed on the fast pyrolysis of biomass using a number of these alkaline catalysts. Auta et al. sought to identify a suitable catalyst for the pyrolysis of OPEFB. In their research conducted using a fixed bed reactor, the efficiencies of potassium carbonate (K_2CO_3), calcium hydroxide $Ca(OH)_2$ and magnesium oxide MgO as pyrolysis catalysts were tested under various reaction conditions. The effects of pyrolysis temperature, N_2 gas flow rate, and the amount of catalyst on the products yield were the primary factors which were evaluated. Among the catalysts tested, $Ca(OH)_2$ with 10 wt% of OPEFB gave

Table 2
Comparison of phenol content of bio-oils derived from conventional and microwave-assisted pyrolysis (non-catalytic and catalytic).

Process	Biomass	Temperature (°C)	Phenol (area%)	References
Fluid bed	PKS	500	28.3	Islam et al. (1999)
Fluid bed	PKS	453	22.1	Kim et al. (2010)
Fluid bed	OPEFB	500	18.1	Sukiran et al. (2009)
Fixed bed	PKS	500	13.4	Abnisa et al. (2011)
Microwave	PKS	500	72.0	Salema and Ani (2012a)
Microwave	SP	400	42.5	Bu et al. (2013)
Microwave	LG	550	45	Bu et al. (2014)
Microwave	PKS	289	30.6	Aziz et al. (2013)
Microwave	SW	390	19.0	Aziz et al. (2013)
Microwave	WS	120	2.0	Budarin et al. (2009)
Microwave	WSD	480	2.0	Borges et al. (2014)
Microwave	CS	490–560	4.3	Borges et al. (2014)

CS: corn stover; OPEFB: oil palm empty fruit bunch; LG: lignin; PKS: palm kernel shells; SP: sawdust pellets; SW: sage waste; WS: wheat straw; WSD; wood sawdust.

the maximum bio-oil yield (42–64 wt%) when processed at 600 °C with a N_2 gas flow rate of 200 mL/min. In GC–MS analysis, phenolic compounds in the bio-oil obtained with $Ca(OH)_2$ increased to 27.7 area% (phenol: 14.6 area%), while acids decreased to 35.2 area%, compared with 16.7 area% of phenolic compounds (phenol: 7.6 area%) and 42.9% acids from bio-oil processed through non-catalytic OPEFB pyrolysis (Auta et al., 2014). $Ca(OH)_2$ was also evaluated as an effective catalyst for the conversion of biomass to phenolic-rich bio-oil in hydrothermal liquefaction (Karagöz et al., 2004). Peng et al. investigated the effects of different amounts (0–20 wt%) of alkaline catalysts (NaOH, KOH, Na_2CO_3 and K_2CO_3) on the production of phenolic compounds from the pyrolysis of lignins (alkali lignin and lignin purified from black liquor) in a fixed bed reactor. The authors found that all alkaline catalysts promoted decarboxylation or decarbonylation, as well as the removal of unsaturated alkyl branch chains. In particular, the strong alkalinity of NaOH and KOH actively facilitated deoxygenation to produce a relatively high amount of simple phenols (80% in the liquid), which were free of methoxyl groups. While the hydroxide catalysts produced more alkylated phenols, the carbonate additives of Na_2CO_3 and K_2CO_3 promoted the production of methoxy-phenols (Peng et al., 2014). The role of NaOH and $Ca(OH)_2$ plus H_2O_2 as pretreatment agents for OPEFB prior to pyrolysis with zeolites was investigated by Misson et al. They reported that the consecutive addition of NaOH and H_2O_2 to OPEFB led to an almost 100% decomposition of OPEFB lignin, while a system operated with $Ca(OH)_2$, and H_2O_2 treatments partially decomposed OPEFB (44%). The pyrolysis of the pretreated OPEFB over 5 wt% Al-MCM-41 and HZSM-5 at 300 °C in a stainless steel reactor resulted in phenolic yields of 90 and 80 wt%, while a 67 wt% yield was achieved for the untreated sample under the same conditions. In this work, they postulated that NaOH pretreatment could lead to the saponification of intermolecular ester bonds crosslinking xylan hemicellulose and other polymeric materials, such as lignin or other hemicelluloses (Misson et al., 2009). Sodium (Na), as an organically bound form or as inorganic salts, was also reported to have a catalytic effect on the pyrolysis of alkali lignin (Guo et al., 2014). A study carried out by Lu et al. showed that the catalytic fast pyrolysis of poplar wood, pine wood, corn stalk, commercial cellulose and xylan treated with K_3PO_4 produced phenolic-rich bio-oils. They performed analytical Py-GC–MS analysis, and reported that K_3PO_4 promoted the decomposition of lignin to form simple phenols (mainly phenol and 2,6-dimethoxyphenol). The contents of phenol and 2,6-dimethoxyphenol in the bio-oils obtained in their study were increased in proportion with the increasing K_3PO_4 content. The maximum values of phenol and 2,6-dimethoxyphenol were 14.3 and 15.2 area%, and the maximum content of total phenolic compounds was over 60 area% where a high K_3PO_4 content was applied. Their work also showed that some phenolic compounds containing hydroxyl and carbonyl groups on the side chain were significantly reduced or completely eliminated in the catalytic process, suggesting that K_3PO_4 promotes dehydroxylation and decarbonylation reactions during lignin pyrolysis. Moreover, they suggested that K_3PO_4 enhances side-chain elimination reactions (Lu et al., 2013). In another study carried out by Zhang et al., using pyrolysis-gas chromatography–mass spectrometry and poplar wood as a feedstock, the catalytic effect of K_3PO_4 on the production of phenolic-rich bio-oil was again confirmed, and the catalytic effects of K_3PO_4, K_2HPO_4, or KH_2PO_4 were compared. The experimental results revealed that each of the three catalysts promoted the formation of phenolic compounds from lignin, and that K_3PO_4 and K_2HPO_4 brought about a higher production of phenols than KH_2PO_4. In the study, the maximal content of the phenolic compounds in the bio-oils was as high as 68.8 area% at 50 wt% K_3PO_4 (Zhang et al., 2014).

Recently, a two-stage catalytic pyrolysis and catalytic upgrading were also investigated for the production of a phenolic-rich bio-oil. In the work of Yoshikawa et al., a two-stage catalytic pyrolysis of lignin was performed in an autoclave reactor using a silica alumina catalyst in a water/1-butanol solution, and subsequently, in a fixed-bed flow reactor over an iron oxide catalyst (denoted as $ZrO_2–Al_2O_3–FeO_x$) which aided the decomposition of lignin constituent monomers and dimers (Yoshikawa et al., 2013). In the first step, the depolymerization of lignin by hydrolysis was conducted to produce lower molecular weight lignin-derived liquids (85–88 Cmol%). In the second step, the lignin-derived liquids were converted into phenolic compounds. With the method, the conversion of methoxy phenol and total recovered fractions of phenolic compounds were 92–94% and 6.6–8.6%, respectively. Mante et al. focused on the defunctionalization of monomeric phenols obtained from kraft lignin. For the purpose, they carried out a lignin pyrolysis using a quartz tube and a micro reactor. The micro reactor was packed with titanium dioxide (TiO_2) to selectively remove hydroxyl, methoxy, carbonyl and carboxyl functionalities from the monomeric phenols flowing from the tube reactor. The experimental results showed that anatase TiO_2 was more selective and active in the defunctionalization of monomeric phenols compared to rutile TiO_2. It was also determined that catechols were the most reactive monomeric phenols to anatase TiO_2, while 4-ethylguaiacol was the least reactive. In their study, over 97% conversion of phenols was achievable at moderate temperatures (550 or 660 °C) and a catalyst/feed ratio of 6.5:1 (Mante et al., 2013).

3.2. Current trend in the separation of phenolic compounds from bio-oil

Typical technologies for the separation of phenolic compounds from bio-oil are not very different from the separation technologies presented in the Section 2.3. Among those technologies, solvent extraction especially using switchable hydrophilicity solvents

(SHSs) and supercritical CO_2, and molecular distillation appear to be very interesting.

Solvent extraction remains a representative separation technology for bio-oil and has also been applied for the separation of phenolic compounds from bio-oils. In an early study, Amen-Chen et al. isolated phenolic compounds from wood tar with the objective of recovering phenol, cresols, guaiacol, 4-methylguaiacol, catechol and syringol. In the study, wood tar was first converted into light oils, and then phenolic compounds were separated from the oil using a five cross-current stage extraction utilizing alkali and organic solvent. The solvent extraction successfully isolated a phenolic fraction, especially under highly alkaline conditions (pH of 12–13) (Amen-Chen et al., 1997). Wang et al. recently conducted a multi-step separation of monophenols and pyrolytic lignin from the water-insoluble phase of bio-oil obtained from the pyrolysis of lauan sawdust, utilizing acid (HCl) and alkaline (NaOH) solutions combined with an organic solvent (CH_2Cl_2). After extraction, filtration, and distillation at each stage, three fractions: a neutral fraction (FA), intermediate phenolic fraction (FB), and final phenolic fraction (FC), could be obtained, along with two filter precipitates, high-molecular-weight pyrolytic lignin (HMWPL) and low-molecular-weight pyrolytic lignin (LMWPL). The authors reported that the relative contents of total phenolic components in FB and FC amounted to 94.4% and 54.3%, respectively. In particular, the content of guaiacols in FB was 48.3%. HMWPL contained predominance of polymers with a molecular weight greater than 1000 g/mol, whereas LMWPL contained more reactive phenolic hydroxyl groups (Wang et al., 2014).

Meanwhile, a new extraction procedure based on switchable solvents has gained much attention for the separation of valuable components from bio-oils. Switchable solvents, which can generally be categorized as switchable polarity solvents, SHSs, and switchable water, are characterized as a reversible switch-ability from a liquid with one set of properties to another that has very different properties, upon application or removal of a trigger (typically CO_2) (Fu et al., 2014). SHSs, therefore, can be defined as solvents that have very little miscibility with water in the absence of CO_2, but complete miscibility with water in the presence of CO_2. The change in miscibility is caused by a chemical reaction of the CO_2 and water with the SHSs, giving a water-soluble bicarbonate salt of the protonated SHSs. SHSs must therefore be sufficiently basic to be protonated by carbonic acid. An example of SHSs is tertiary amines, such as N,N-dimethylcyclohexylamine, which is poorly miscible in water without CO_2, but become miscible with water in the presence of CO_2 (1 atm). SHSs are suitable for the extraction of phenolic compounds from bio-oil, and this is likely due to their alkalinity enabling the extraction of phenolic compounds from bio-oil. Furthermore, SHSs can be removed from the extracted products without distillation (Jessop et al., 2011). Fu et al. studied an extraction method based on SHSs for the extraction of phenolic compounds from a bio-oil derived from the pyrolysis of a lignin. They first carried out a microwave-assisted pyrolysis of a softwood kraft lignin to obtain a bio-oil, which was mixed with N,N-dimethylcyclohexylamine. After the switching process was complete, a low-polarity fraction and phenolic-rich fraction could be obtained. The original bio-oil and its fractions after separation were analyzed by quantitative NMR spectroscopy. The analysis revealed that phenolic compounds were concentrated in one fraction, which contained 72% of the guaiacol and 70% of the 4-methylguaiacol present in the original bio-oil. In the experiments, 91% of the solvent SHS could be recovered after extraction (Fu et al., 2014).

Supercritical CO_2 extraction, which has been mainly applied in food, flavor, fragrance and pharmaceutical industries, was adopted for a feasibility study of the separation of phenol-rich oil from bio-oil by Patel et al. In the study, the supercritical CO_2 extraction was performed with bio-oils derived from sugarcane bagasse and cashew nut shells with a pressure range of 120–300 bar, temperature range of 30–60 °C and supercritical CO_2 mass flow rates of 0.7–1.2 kg/h. A phenolic-rich oil was extracted, the concentration of extracted phenolic compounds of which was about 72%, with a total oil yield of 15%. Cardanol-rich oils were also extracted from the bio-oils derived from cashew nut shells. A higher concentration of cardanol (86%) was observed in the extract, along with approximately 5% phenols ($\sim$5%) (Patel et al., 2011).

In addition to conventional distillation technologies, which have a number of limitations in the separation of phenolic compounds from bio-oil, a new distillation approach, molecular distillation, has recently been applied. Guo et al. carried out a two-step molecular distillation of a bio-oil, which was pretreated by centrifugation, filtration and traditional vacuum distillation at 50 °C. The two-step distillation was conducted as follows: first, the vapor compounds generated during molecular distillation process at 1600 Pa were condensed using an internal condenser, giving rise to a distilled fraction. The nonvolatile bio-oil flowed down the evaporator surface and was collected as a residual fraction. The residual fraction was then used as a feed material for the second distillation process. The two-step molecular distillation generated two distilled fractions (DF-1 and DF-2) and two residual fractions (RF-1 and RF-2). They reported that the yield of distilled fraction obtained after the first molecular distillation process (DF-1) was 26.4 wt% and the yield of the second distilled fraction (DF-2) was 22.6 wt%. Mono- and diphenols were the most abundant chemicals in RF-1 and RF-2. The distillation results revealed that acids, ketones, furans and ethers were easily separated from the bio-oil, while aldehydes, diphenols and sugars were somewhat more difficult to separate (Guo et al., 2010).

3.3. Application of phenolic-rich bio-oil

Because bio-oil contains lots of simple phenols and oligomeric polyphenols (or pyrolytic lignin), the application of bio-oil is dependent on which fraction is used. A very useful application way for phenolic compounds in bio-oil is to recover simple phenols from bio-oil, because they are valuable chemicals which are suitable for a broad range of applications. Simple phenols can be used in many industries, such as fine chemicals, pharmaceuticals, food processing, and resin manufacturing. To the best of our knowledge, there have been no reports of the attempted recovery and use of simple phenols from bio-oil for commercial products, and this is likely due to the difficulty in separating simple phenols. In contrast, efforts have been made by a number of research groups to apply pyrolytic lignin as a substitute for fossil phenols in phenolic resins, and there is currently at least one trial use of pyrolytic lignin as a replacement for fossil bitumen (ex. asphalt binder) (Fini et al., 2011). Phenolic resins are normally synthesized by acid or base catalyzed reactions between phenols and aldehydes. Phenol-formaldehyde (PF) resin, a representative phenolic resin, is obtained by the reaction of phenol or substituted phenols with formaldehyde, leading to the formation of novolacs (thermoplastic) or resoles (thermosetting), respectively. Phenolic resins are widely used in many industries, including electronic laminating and wood composite industries. In particular, they have been traditionally used as binders of wood composite products, such as plywood and oriented strand board (OSB). Phenolic-rich bio-oil can usually replace petroleum-derived phenol in phenolic resins in one of the following three ways: (1) using phenolic-rich oil (or pyrolytic lignin) obtained after fractionation of bio-oil, (2) using pyrolysis oil from pyrolysis of lignin or (3) using a whole bio-oil. To obtain a phenolic-rich oil (or pyrolytic lignin), fractionation of a whole bio-oil is usually conducted using various methods, such as precipitation in water and extraction and distillation. Pyrolysis of lignin yields a phenolic-rich bio-oil that can be used in the synthesis of phenolic resins without any fractionation. The use of a whole bio-oil is very interesting, because it has the potential for partial replacement of formaldehyde used for the PF resin synthesis by aldehydes of the whole bio-oil.

Although bio-oils containing a high content of phenolic compounds have a strong potential for the replacement of fossil phenol, they suffer from a relatively low reactivity in the phenolic resin synthesis, as typical bio-oil contains a low concentration of reactive phenol, and the mixture of phenolic compounds (primarily alkylated phenol and aromatic ethers) in bio-oils is less reactive than pure phenol. In the early of 2000s, intensive research on the synthesis of wood adhesives was carried out, using softwood bark residues bio-oil produced by the vacuum pyrolysis. In 2009, Sukhbaatar et al. again explored the possibility of using pyrolytic lignin as a binder for OSB. In their study, they first separated a lignin fraction (25 wt% yield on bio-oil weight), using water and methanol from bio-oil produced by fast pyrolysis of pine wood in an auger reactor. PF resins were produced using the isolated pyrolytic lignin at 30%, 40%, and 50% phenol replacement levels. They calculated that up to about 40% incorporation of pyrolytic lignin did not lower the performance of the synthesized PF resin (Sukhbaatar et al., 2009). Very recently, Chaouch et al. reported the use of a bio-oil from whole-tree feedstock in resol-type PF resins. In their work, bio-based PF resins were formulated, partially substituting phenol by bio-oils produced from two Canadian whole-tree species. The phenol replacement levels were 25%, 50%, and 75%, and the results obtained showed that the physical and mechanical properties of bio-based PF resins were strongly influenced by the substitution level of phenol. A substitution degree up to 50 wt% provided an equal or superior reactivity and performance to those of the pure PF resin (Chaouch et al., 2014). Mao et al. investigated the feasibility of incorporating the bio-oil as part of a polymeric diphenylmethane diisocyanate (pMDI) binder system for flakeboard production. In their study, a fraction of the bio-oil produced by the fast pyrolysis of pine wood was mixed with acetone and pMDI to make a resin. This resin was blended and sprayed onto wood flakes, after which flakeboard was manufactured using a hot press. The mechanical and physical properties of flakeboard bonded with different resin formulations were examined. They found that at 7 wt% resin content, the bonding properties of flakeboards formulated with an adhesive consisting of 25% bio-oil was comparable to that manufactured using pure pMDI (Mao et al., 2011).

4. Conclusion

This review highlights the high amount of phenolic compounds that can be obtained from biomass using alkaline catalysts and microwave-assisted system with activated carbon. In particular, the phenol concentration in a bio-oil derived from a palm residue was very high with a value of 85 area%. New separation technologies, such as extraction using supercritical CO_2 and switchable hydrophilicity solvents, and molecular distillation, appeared to be promising methods for the separation of phenolic compounds. Finally, the application of phenolic-rich bio-oils to the synthesis of phenol-formaldehyde resin shows their strong potential for the replacement of phenols sourced from fossil fuels.

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